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LABORATORY EVALUATION OF TUNABLE ATOMIC LINE MOLECULAR SPECTROMETERS FOR BENZENE ANALYSIS

by

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16. ABSTRACT

Tunable Atomic Line Molecular Spectroscopy (TALMS) is a high resolution, differential absorption technique used in the ultraviolet region. Under Interagency Agreements EPA-80-D-X1014 and AD-89-F-2A008 with Lawrence Berkeley Laboratory, two prototype TALMS instruments were designed, constructed, and delivered to the U. S. EPA at Research Triangle Park, North Carolina. TALMS I was a large laboratory instrument designed to demonstrate the feasibility of TALMS detection of toxic organic compounds. TALMS II was a more compact monitor for benzene designed for possible field applications. Both instruments were evaluated in the laboratory for performance characteristics in the analysis of benzene using the 253.7 nm mercury line. The tests included detection limit, precision, effect of temperature (TALMS I), effect of pressure (TALMS II), and interferences from organic compounds other than benzene.

The prototype instruments evaluated can detect benzene precisely above the detection limit of 6 μg. The apparent interferences from toluene and pyridine are relatively small and may be artifacts which can be eliminated with improvements in electronic signal processing. It was recommended that changes to the sample cell and electronics be made to improve the detection limit and that extension of the capabilities of TALMS to other organic compounds be made.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Analysis of organic compounds in the atmosphere is a difficult task requiring a variety of analytical techniques to ensure that identification and quantification are valid. The environmental analyst requires methods that are precise, accurate and easy to implement. This study is concerned with the evaluation of new instruments which utilize the information available in the high resolution absorption spectra of organic compounds in the ultraviolet and visible regions. The use of these instruments in the analysis of organic compounds may greatly improve the ability of the analyst to produce valid results.

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ABSTRACT

Tunable Atomic Line Molecular Spectroscopy (TALMS) is a high resolution, differential absorption technique used in the ultraviolet region which was recently developed at Lawrence Berkeley Laboratory. Under Interagency Agreements EPA-80-D-X1014 and AD-89-F-2A008 with Lawrence Berkeley Laboratory, prototype TALMS instruments were designed, constructed, and delivered to Research Triangle Park, North Carolina. TALMS I was a large laboratory instrument designed to demonstrate the feasibility of TALMS detection of toxic organic compounds. TALMS II was a more compact monitor for benzene designed for possible field applications. Both instruments were evaluated in the laboratory for performance characteristics in the analysis of benzene using the 253.7 nm mercury line. The tests included detection limit, precision, effect of temperature (TALMS I), effect of pressure (TALMS II), and interferences from organic compounds other than benzene.

The tests on TALMS I gave a detection limit of 35 μg benzene with a median precision of 20%, relative standard deviation. Apparent negative interferences on benzene were found for o-xylene, pyridine, and toluene of 2.8, 23, and 16%, relative to an equal volume of benzene. For a change in temperature from 27 to 160°C an increase in signal was found for benzene, pyridine, and toluene of 21, 50, and 57%, respectively. TALMS I had a moderate amount of downtime during these tests.

The evaluation of TALMS II gave a detection limit of 6 μg benzene with a median precision of 7.2%, relative standard deviation. Apparent negative interferences on benzene were found for pyridine, toluene, chlorobenzene, and styrene of 7.0, 1.7, 0.5, and 5.2%, respectively. Since the interferences decreased from those found with TALMS I, there is a possibility that these are artifacts of the signal processing electronics. The study of pressure in the sample cell on TALMS signal showed a decrease in signal intensity of 8% at 66 torr and 46% at 636 torr, relative to the signal at 3 torr. This effect must be allowed for in calibration and sample analysis. After addition of an automatic gain control unit, very few problems were encountered with TALMS II.

It was concluded that the prototype instruments evaluated can detect benzene above the detection limit with good precision. However, the relatively high detection limit of 6 μg precludes the use of the instrument for direct ambient air analysis. The apparent interferences are relatively small and may be artifacts which can be eliminated with improvements in electronic signal processing. It was recommended that changes to the sample cell and electronics be made to improve the detection limit and that extension of the capabilities of TALMS to other organic compounds be made. Sample preconcentration techniques should also be used with the instrument.

This report covers a period from December, 1981, to December, 1983, and work was completed as of November, 1983.

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SECTION 1

INTRODUCTION

Effective monitoring of air pollution requires the ability to determine a large variety of toxic organic species at low concentrations. The identification and quantification of almost all organic compounds in the air are presently accomplished using some type of chromatographic technique, e.g., gas chromatography (GC), GC - mass spectrometry (GC-MS), or high performance liquid chromatography (HPLC). The methods are time-consuming, frequently not very selective, and in the case of GC/MS, require expensive equipment. A selective technique that depends on high resolution spectrometric principles would be faster and reduce the likelihood of incorrect qualitative analysis.

An analytical technique called Tunable Atomic Line Molecular Spectroscopy (TALMS) has been recently developed at Lawrence Berkeley Laboratory (1). TALMS is essentially a high resolution, differential absorption spectroscopic technique. It is performed by splitting a source atomic emission spectral line into components with a magnetic field (Zeeman effect). A differential measurement is made between the absorption of a Zeeman component (or components) magnetically tuned to match a sharp analyte absorption feature and an unmatched Zeeman reference component(s). The sharp features in the absorption spectra of the organic compounds are due to rotational-vibrational fine structure in the electronic transitions. The difference in polarization between the split Zeeman components permits the matching and nonmatching wavelengths to be alternately selected and the absorption measured very rapidly with an electro-optical device called a Current Controlled Retardation Plate. The line matching is illustrated in Figure 1 for a magnetic field parallel to the direction of light emission. The wavelength of the unsplit atomic line (at zero magnetic field) is indicated by the dashed line. The splitting shown is dependent upon magnetic field strength. The Zeeman component labeled M=+1 is tuned with the magnetic field to match the electronic-vibrational-rotational line of a specified molecule in the sample. The TALM spectrometer detects the difference in absorption between the M=+1 (right circular polarization) and the M=-1 (left circular polarization) reference Zeeman components. The differential absorption is proportional to the amount of molecular species whose absorption line matches the tuned M=+1 component(s) of the source lamp. Therefore, calibration curves can be established following Beer's law.

TALMS is a high resolution (high selectivity) absorption spectroscopic technique. The high resolution is due to the narrow width of the atomic probe line, ca. 0.1 cm^{-1}, the position of which can be shifted by changing the magnetic field strength. The high resolution available has been demonstrated for formaldehyde (2). TALMS is capable of the measurement of a large number of organic compounds with high selectivity. The number of

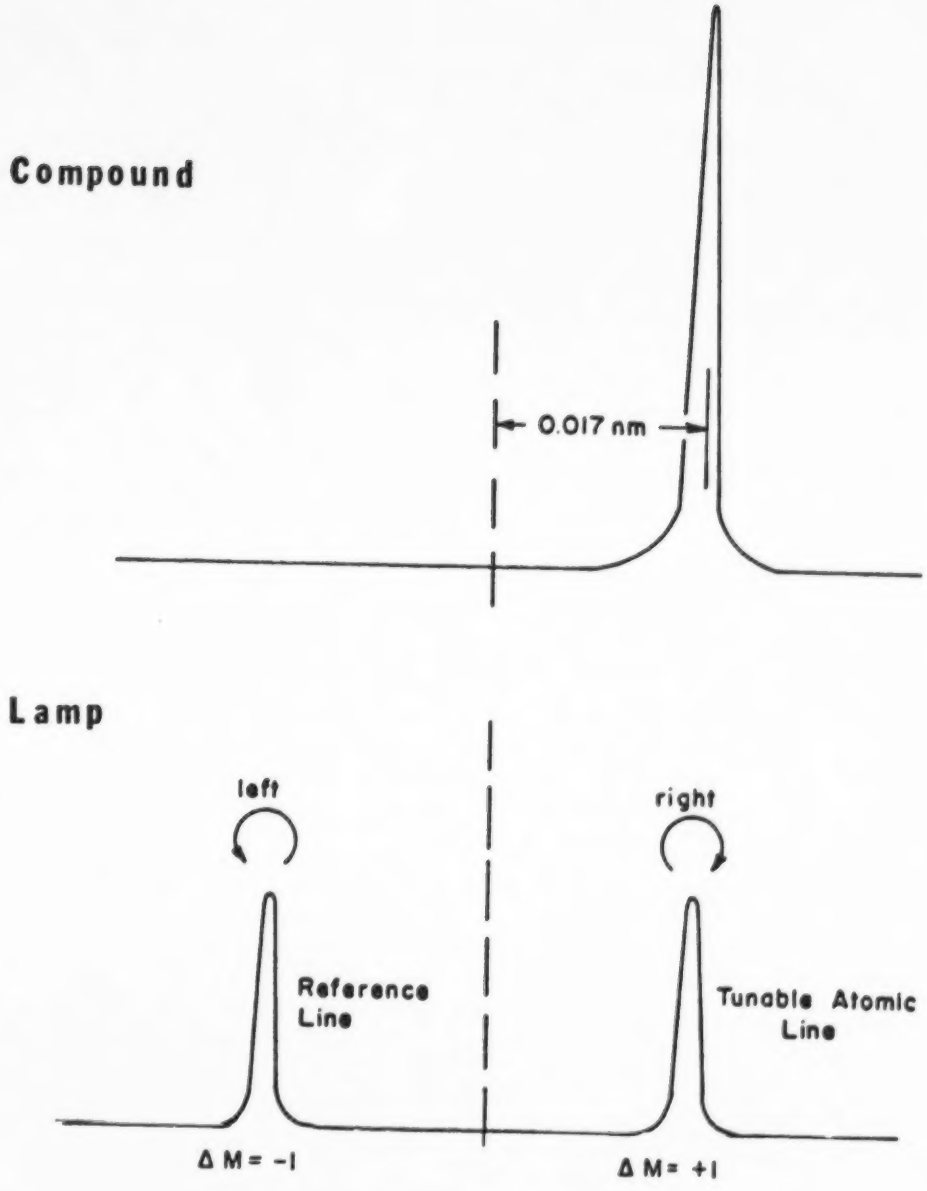

Figure 1. Tunable atomic line molecular spectroscopy.

compounds that can be detected is limited only by the presence of narrow, pseudo line structure in the absorption spectrum of the compound in the gas phase and the matching of an appropriate atomic emission line to this feature.

TALMS has a number of advantages as an analytical technique. It is a direct analysis technique requiring very little sample handling or preparation. Another feature of TALMS is its essential freedom from background interference. Since the difference in wavelength between the Zeeman components of the source emission line is typically 0.04 nm, any particle scattering or semi-continuous absorption will effect both components equally. Therefore, the differential absorption measurement will remove this interference from the total signal. The high resolution attainable with TALMS should result in high selectivity and unambiguous qualitative identification of compounds.

As a result of Interagency Agreements EPA-80-D-X1014 and AD-89-F-2A008 with Lawrence Berkeley Laboratory, TALMS instruments were designed, constructed, and delivered to the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, North Carolina. Two prototype instruments were delivered, a laboratory instrument (TALMS I) and a benzene monitor (TALMS II). Details of the design, construction, and preliminary evaluation of the instruments are given in previously published reports (3,4). Both of these instruments were evaluated in the EMSL laboratory for performance characteristics. This report is concerned with these laboratory evaluations.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

TALMS I, a single beam system, was designed and constructed as a bulky prototype laboratory instrument to demonstrate the feasibility of analysis of toxic organic compounds by Tunable Atomic Line Molecular Spectroscopy. It was supplied with a mercury lamp and was evaluated for benzene detection and analysis. After initial problems with the squeezer, which was later replaced, and experience acquired by the EPA operator; the instrument operated satisfactorily. The precision of analysis was fair with a median of 20%, relative standard deviation, but the main problem for ambient benzene analysis was the detection limit of 35 μg. Also, somewhat surprising were the apparent interferences from pyridine, o-xylene, and toluene. Since TALMS is a high resolution technique, this is unexpected. Evidence collected with TALMS II indicates that these interferences may be artifacts of the signal processing system. Another surprising result was the increase in TALMS signal with increase in temperature for benzene, toluene, and pyridine.

TALMS II was designed and constructed as a compact monitor for benzene. It was much smaller than TALMS I and used a dual optical system to compensate for lamp and electronics drift. Except for an initial problem leading to erroneous interferences, which was corrected by the addition of an automatic gain control circuit, the instrument performed very well. The precision with a median of 7%, relative standard deviation, was good, probably due to the dual beam system. The detection limit of 6 μg was much better than that for TALMS I, although not adequate for direct ambient benzene monitoring. The interferences found for toluene and pyridine, from 1.7 to 7%, were much less than the corresponding values for TALMS I. This is an indication that the apparent interferences may be artifacts introduced by inaccuracies in the signal processing electronics. The effect of pressure on the TALMS signal is an important problem and must be accounted for in calibration and analysis of samples.

At the present stage of development the TALMS II instrument cannot be used for direct analysis of ambient benzene due to its detection limit of 6 μg. It is recommended that further work be done to evaluate the use of concentration methods, e.g., solid sorbents or cryogenic concentration, with the TALMS monitors. Also further extramural studies should be funded to locate more intense analysis lines for benzene, e.g., the Co line at 252.8 nm (5), and other toxic organic compounds. A monochromator and electromagnet should be added to TALMS II to extend its capabilities, and a sample cell with smaller volume should be added. A study should be conducted at Lawrence Berkeley Laboratory to find the cause of the temperature effect, which might be used to enhance the detection limit. Some of the recommended changes to TALMS II have been made in a later version, TALMS III, which has been delivered to EMSL, Research Triangle Park, North Carolina in December, 1983.

SECTION 3

EVALUATION OF TALMS I

An overview of the TALMS measurement process is illustrated in Figure 2. An appropriate atomic emission lamp is housed in a magnet which produces Zeeman splitting into components of the emission line. The splitting is directly proportional to the magnetic field strength. The Zeeman components, which have different polarizations, are absorbed by the gas phase sample contained in a cell. The differently polarized components are detected alternately in time by the selector (polarizer and squeezer) and detected with lock-in amplifiers and photomultipliers. The monochromator acts as a blocking filter to pass only the desired atomic emission lines from the lamp.

EQUIPMENT

The TALMS instrumentation can be constructed in two configurations, parallel or perpendicular, referring to the alignment of the direction of light propagation and magnetic field direction. In both TALMS I and II, the perpendicular configuration has been used since the parallel configuration requires drilling a hole through the magnet pole piece. The perpendicular configuration also is best for benzene detection.

TALMS I was designed as a multipurpose, laboratory instrument. It is 58 in (147 cm) long, 33 in (84 cm) wide, 27 in (69 cm) high, and quite heavy. However, it fits on top of an ordinary desk. A photograph of TALMS I is given in Figure 3. The design of this instrument is best described by considering the main components in the optical path. See Figure 4 for a block diagram. The magnet in this figure has been rotated 90° to show the lamp position. The main components are the lamp, the magnet that contains it, the current controlled retardation plate (squeezer), polarizer, monochromator, absorption cell, and detector with signal processing electronics.

The lamp utilized for the TALMS I work was a sealed low frequency mercury discharge lamp, which essentially consists of a mercury Pen-Ray lamp with a wire heater wound about the tube. This lamp was contained in an aluminum cartridge with self-contained iron pole pieces for the magnet. The lamp emits only a small number of lines, including the 253.7 nm line, making it useful for specific analysis. The advantage of this lamp is its extremely long operating life and its high intensity resonance lines. The lamp is driven at 15 KHz by a power module.

A permanent magnet with the source lamp mounted between the pole pieces in the perpendicular configuration was used to produce the Zeeman effect. A pole gap of 6 mm was used for the cartridge lamps. Measurements of the field strength at the lamp gave 8.4 kilogauss.

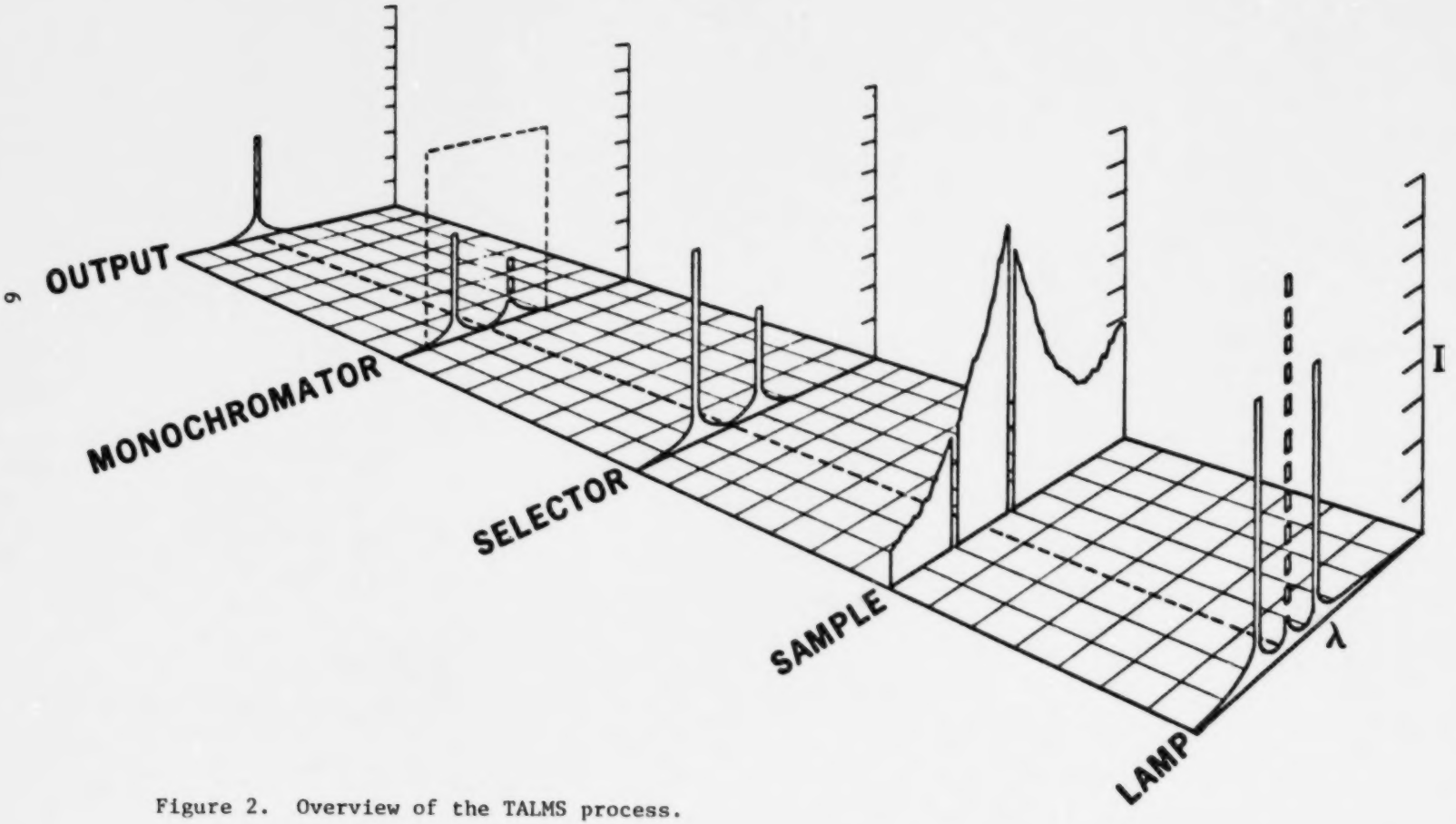

Figure 2. Overview of the TALMS process.

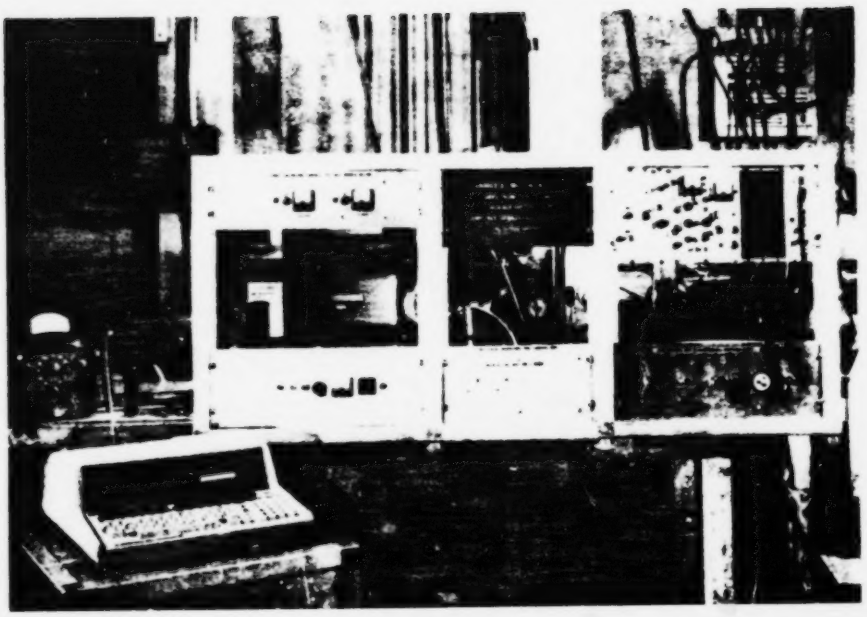

Figure 3. TALMS I instrumentation.

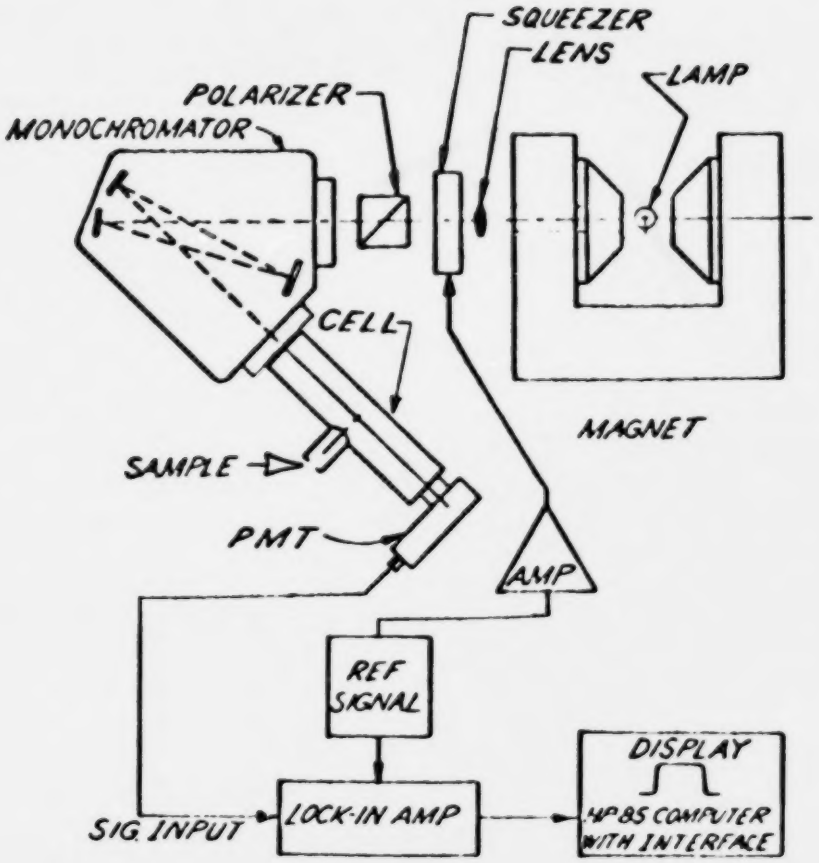

Figure 4. Block diagram of TALMS I.

The current controlled retardation plate, or squeezer, consisted of a quartz crystal mounted between the arms of a "C" electromagnet. As the quartz was subjected to cyclic mechanical stress via an audio (ca.70 Hz) frequency AC signal, it functioned as an electro-optical shutter, passing alternately the matched and the unmatched Zeeman components. A polarizer was mounted in the optical path at such an angle of rotation that the only light transmitted was polarized at an angle of 45 degrees to the direction of stress in the squeezer.

Because of the intended multipurpose use of TALMS I, a McPherson Model 218, 0.3 meter scanning monochromator was used in this system. This instrument also possessed a large acceptance angle because of its short focal length. The spectral range covered was 105 to 1,000 nm, and the spectrum was dispersed with a 1200 G/mm grating. The slit width was set at 300 microns throughout this study.

The cell consisted of quartz windows fitted to the ends of a Varian nipple and con-flat system. The path length was 16 cm, and the volume was 135 ml. A septum for sample injection was fitted to a tee connected into the inlet line to the cell. The cell was connected through a simple plumbing system to solenoid valves allowing evacuation and sample admission. The pump used for sample evacuation was a Sac Vac 8803 single stage, 25 L/min, portable, rotary oil pump.

The detector used was a Hamamatsu R928 photomultiplier tube (PMT). The PMT mounting and dynode resistor net were of conventional design.

Appropriate electronic modules were used to operate the above units, furnish power, and process the signal. A light driver module furnished power to sustain the light discharge and provide heat for the lamp. The squeezer was controlled by the variable frequency driver and the D.C. clamp control. The photomultiplier tube was powered by the PMT high voltage power supply. The signal flow is shown in Figure 5. A lock-in amplifier operating at the squeezer frequency was used to detect and amplify the signal. The signal was processed by a log amplifier and sent to the computer.

The computer was an HP-85 with IEEE interface and 6942A multiprogrammer bin. During analysis, it operated the TALMS and collected data to be processed later. The software used for data processing is described below.

OPERATIONAL SOFTWARE

The HP-85 program furnished by Lawrence Berkeley Laboratory allowed for computer control of valves, number of times sampled, time between samples and ratio of pumping to recording time. Data were presented as two series of dots on an x,y plot, one curve being the TALMS signal and the other the total PMT response or total absorbance. Scale modification was allowed as well as an irreversible curve suppression. Except for software patches to prevent error messages and to make curve suppression reversible, this portion of the program was not changed.

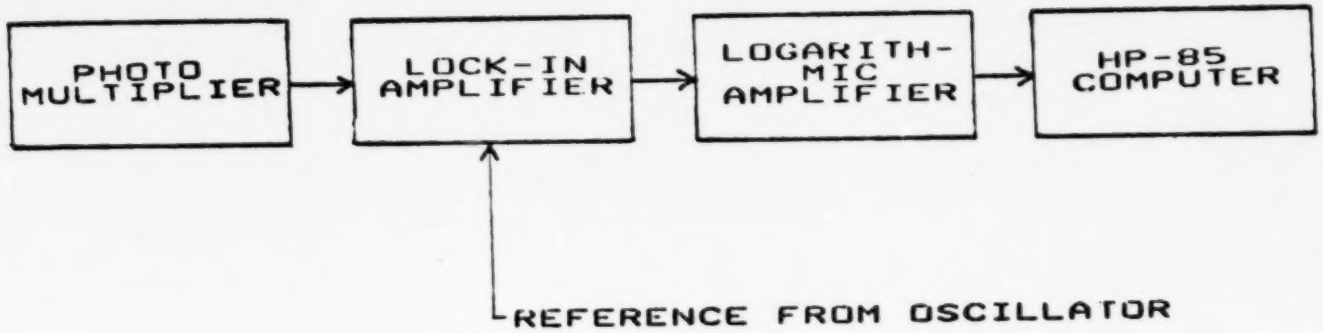

Figure 5. Signal processing electronics for TALMS I.

Several new features were added by one of the authors (RH). Data points were stored as read, a five point running average was made before plotting, and a tenth of the points were printed for reference. When sampling was completed, the operator could choose two segments of the curve, (for example, one while pumping and one with the sample in the cell); and the computer would then print and plot the average and give the maximum, minimum, and standard deviation of each segment. It would compare the average of the two segments, giving the arithmetic difference and its standard deviation. An outline of the computer sequence follows.

1. HOW MANY SAMPLES (<257)?

This is a request for the number of times you wish to test the PMT signal. An answer of 50 or 100 is usually satisfactory.

2. TIME BETWEEN SAMPLES (minimum time is >.05 sec)?

Testing the PMT signal actually consists of discharging a capacitor. Sufficient time must be allowed for the capacitor to recharge, but too much time allows noise signals to build up. A good compromise is 0.1 second.

3. WHAT FRACTION OF RECORDING TIME IS EVACUATION TIME?

This is, during what portion of the whole analysis sequence will the pump operate before the sample is admitted to the cell? Enough time must be allowed to establish a good baseline, and enough time must remain for the sample to equilibrate and give a stable TALMS signal. A response of 0.3 or 0.4 (30 to 40%) usually is good.

4. The data gathering sequence starts. Data points are stored. The vacuum pump valve is open to the cell.

5. The sample is injected when the pump valve closes. Data points continue to be collected and stored.

6. When the run is over, the vacuum pump valve opens to permit evacuation of the cell. Dialog recommences.

7. MODIFY DISPLAY?

a. "Y", go to step 8.
b. "N", go to step 12.

8. DISPLAY MODIFICATION

Curve suppression: enter 1
Scale change: enter 2
a. "1", go to step 9.
b. "2", go to step 10.

9. WHICH CURVE DO YOU WISH TO SUPPRESS (1 or 2)?

a. "1", Suppress the TALMS curve and go to step 10.
b. "2", Suppress total absorbance curve, go to step 10.

10. WHAT VERTICAL SCALE?

Use a value that shows the curve to the best advantage. The actual scale plotted will be 1.2 times the requested value. The replot will be a five point running average. If only a smoothing of the curve is needed, the response should be 1024, which is the original value. (Note that display modification or curve smoothing procedures are graphic enhancements only and do not alter the final sample calculation.)

11. MORE DISPLAY?

a. "Y", go to step 8.
b. "N", go to step 12.

12. The computer now outputs about 10% of the TALMS data points for reference in answering 14 and 15.

13. AVERAGE SEGMENTS?

a. "Y", go to 14.
b. "N", go to 17 (output plot and END)

14. DEFINE FIRST SEGMENT (baseline)

Average from #? thru #?
For example, if 50 points were sampled with a 30% pump time, an appropriate answer might be "1, 15".

15. DEFINE 2ND SEGMENT (sample)

Average from #? thru #?
Given the same case as in 14, "31, 45" would suffice.

16. The computer outputs the results of the calculations.

17. The printer outputs the plot as amended by the operator.

18. END

INSTRUMENT TUNE-UP PROCEDURES

Once a day, the following procedures should be followed. If the power to the instrument has been off for an extended time period, then the procedures also should be followed. The appropriate controls are shown in Figure 6.

1. Set monochromator to appropriate wavelength, 253.7 nm for benzene if using an Hg lamp.

2. Adjust PMT output voltage to less than 1 volt.

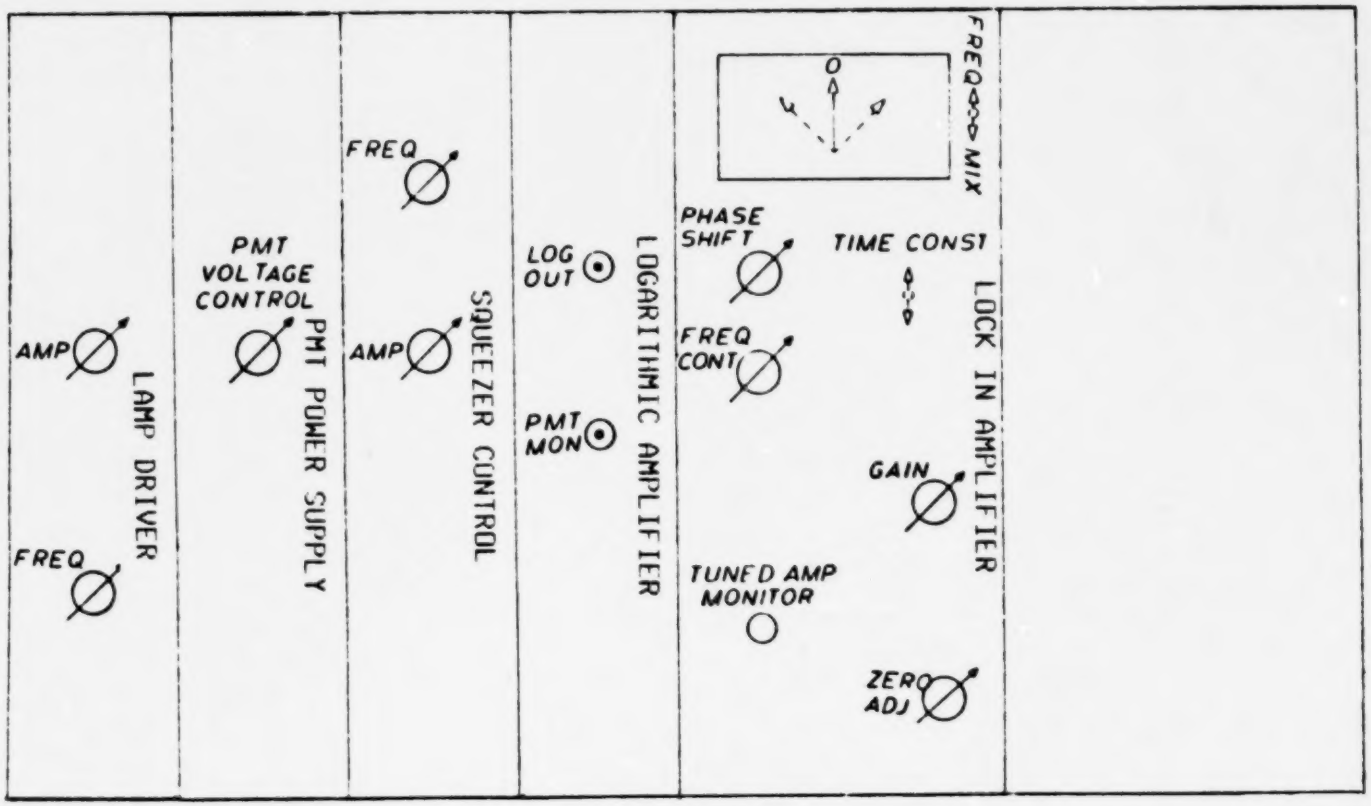

Figure 6. Electronic module controls for TALMS I.

3. Set the Lamp Driver Amplitude knob just high enough to avoid lamp flicker.

4. Squeezer adjustment

a. Set the D.C. clamp current to 0.6 ampere.
b. Adjust the frequency knob on the Squeezer Control Module until a slight chatter is audible.
c. Place a linear polarizer in front of the squeezer.
d. Monitor the PMT output with an oscilloscope. Increase gain on the scope until a sine wave is evident.
e. Adjust the D.C. clamp current and frequency control knobs to obtain maximum peak to peak amplitude consistent with a good wave form.

5. Lock in amplifier adjustment.

a. Attach an oscilloscope lead to the Mixer/Freq output of the lock in amplifier.
b. Set the Freq/Mixer switch to Freq. The CRT should show a sine wave.
c. Adjust the frequency knob to get maximum peak amplitude of the sine wave.
d. Set the Freq/Mixer switch to Mixer.
e. Adjust the phase shift knob to obtain a full wave rectified pattern.

6. Remove the extra polarizer.

7. Set the lock-in gain control to about 0.1.

8. Adjust the zero knob to set the meter to a barely positive signal on the D.C. scale.

If an inverted TALMS signal should occur, such as a negative response to benzene when positive is expected; go back to step 5.e and reverse the wave form.

ANALYSIS PROCEDURES

Calibration

The calibration procedure utilizes the injection of a known volume of gas at equilibrium at a fixed temperature with the volatile liquid. The absolute amount of analyte injected, e.g. benzene, can be calculated from the vapor pressure and the temperature. A few milliliters of the liquid, e.g. benzene, to be tested were placed in a flask containing a few glass beads and a magnetic spin bar and equipped with a thermometer. The flask was covered with a septum cap. Before sampling, the bottle was placed on a magnetic stirrer, and the bar spun rapidly enough to cause the beads to disperse the liquid throughout the air in the bottle, thus assuring saturation of the vapor. A sample was withdrawn after waiting for any suspended liquid droplets to fall. Before sampling again, makeup air should

be injected into the bottle to replace that withdrawn. For benzene, the mass (m) injected per mL (V) headspace sampled, is given by the following equation:

$$m/V\ (mg/mL) = \frac{V.P. \times Mol.Wt}{R \times T(K)} = \frac{V.P.\ (atm) \times 78.1}{0.0821\ T(K)} = \frac{951\ V.P.}{T(K)}$$

where $\log_{10}$ V.P. (torr) = 7.969-1787/T(K).

At a temperature of 72°F (22.2C or 295.4 K), m/V for benzene is 351 µg/mL.

Assuming that instrument tune-up and cell evacuation has been accomplished, the calibration procedure was as follows:

1. A sample was withdrawn from the calibration flask.

2. The run sequence was initiated on the computer. Pumping continued on the previously evacuated sample cell. The computer made periodic readings of the TALMS background signal.

3. The sample was injected immediately after the pump valve closed. The computer continued monitoring the TALMS signal. After equilibrium was reached, the response curve flattened.

4. After the run was completed, the pump valve opened, and the cell was again evacuated.

5. The operator selects two portions of the TALMS curve, one while the pump is on (cell empty) and the other during the flat portion of the response curve. Both segments are averaged, statistically tested, and then the difference is calculated.

6. Other samples of differing sizes are introduced, and the procedure repeated from steps 1-6 as desired.

7. When all calibration runs are completed, an analytical curve can be obtained by plotting the TALMS signal vs. the measured volume of gas injected. A linear least squares fit to the data can also be obtained.

8. From the vapor pressure of the analyte at the measured room temperature, the actual mass of material in the cell could be calculated from the equations given above. Then a calibration curve can be constructed as mass injected vs. TALMS signal or a linear least squares fit to the data can be obtained.

Analysis

The procedure for analysis of a gas sample is the same as that given in steps 2 through 5 of the calibration routine. After the sample is analyzed, the mass of analyte in the injected sample may be calculated from the curve or least squares fit generated in the calibration procedure. The concentration of the original sample is obtained by dividing the mass found

by the volume of sample injected. Since the cell volume is 135 mL, this is the volume to be used for samples which fill the cell completely.

RESULTS AND DISCUSSION

All of the tests performed on TALMS I were made with a mercury lamp and the monochromator set at the 253.7 nm Hg line. This line has been shown to give a good match with a sharp rotational-vibrational feature in the molecular absorption spectrum of gas phase benzene (1,4). This absorption feature is shown in Figure 7. The high resolution absorption spectrum of benzene (3,4) is shown as a function of magnetic field splitting (kG) relative to the zero field position at 253.7 nm. Also shown are the relative TALMS signals (arbitrary units) calculated for benzene as a function of magnetic field strength for both the perpendicular and parallel configurations. The perpendicular configuration gives a higher benzene TALMS signal for a given magnetic field strength, and this configuration was used throughout the tests. The field strength was 8.4 kG during these tests.

Evaluation tests were performed on TALMS I for detection limit; precision; calibration curve linearity and stability; interferences by other organic compounds; and effects of temperature. The early tests were performed without knowing that the squeezer was not operating properly. It was later replaced, and the tests were repeated.

The instrumental detection limit was determined by repeatedly injecting decreasing volumes of benzene headspace vapor ranging from 1 to 0.2 mL (350 to 70 μg) in volume. The total signal for each injection was then pairwise t-tested vs. the background signal obtained with an empty cell. The resulting data are given in Table 1. The 0.2 mL volume, which was the smallest volume available, was significantly different at the 99.5% probability level from the background. Defining the detection limit as one-half this amount yields a mass of 35 μg. The relative standard deviation (precision) near the detection limit ranged from 17-54% with a median of 31%. At the higher level of 350 μg, the precision improved to a range of 5 to 24% with a median of 19%. Because of the undetected squeezer problem which was repaired in October, the later data (November) are more indicative of the true performance of the instrument yielding an overall precision of 5 to 36%, relative standard deviation, with a median of 20%.

The slopes and correlation coefficients for calibration runs are listed in Table 2. For each run four to six different concentrations were injected in the range of 175 to 3500 μg. The slopes of the calibration curves, where the curves were expressed as volume (Y) vs. signal (X), were from 0.024 to 0.083 with a median of 0.039. The linearities of the curves, as measured by the correlation coefficients for a linear fit, were from 0.97 to 1.00, with a median of 0.993. Generally, the curves with the largest span of benzene injected gave the higher correlation coefficients.

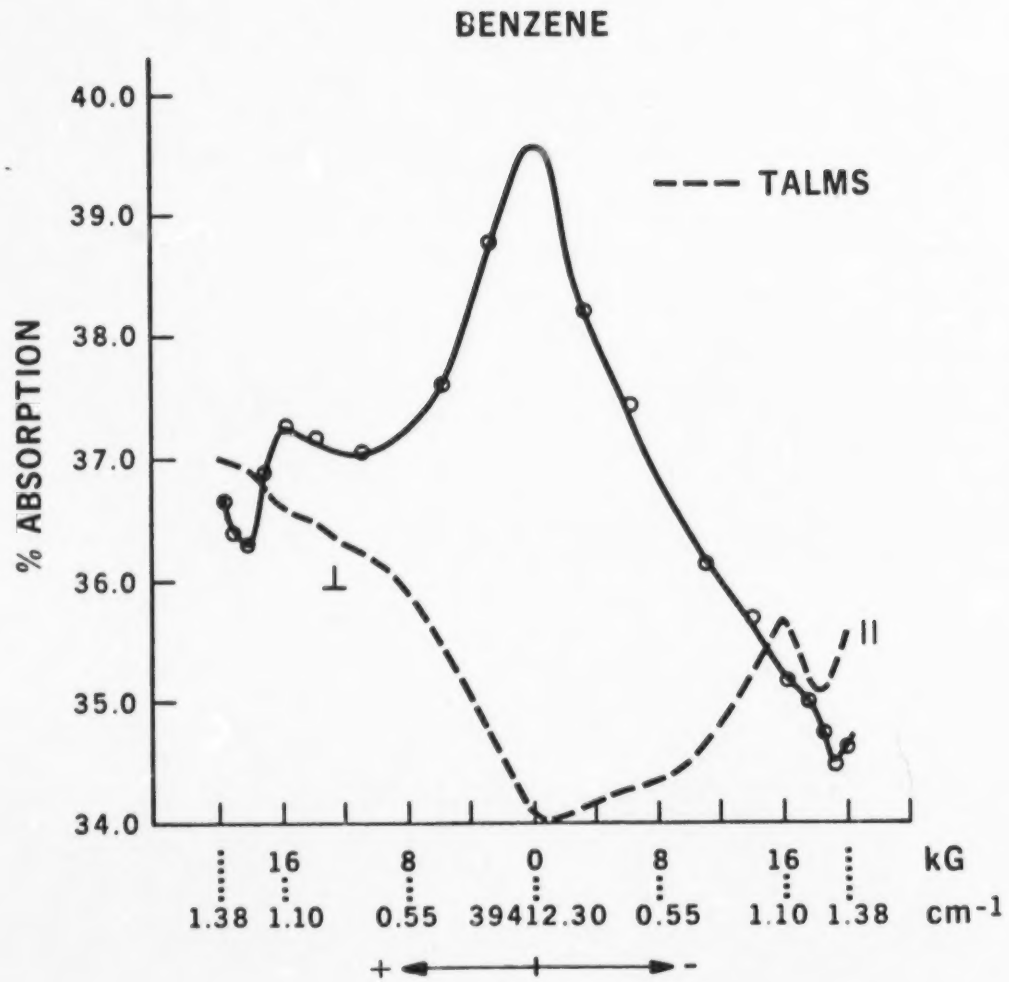

Figure 7. TALMS benzene absorption at 253.6 nm Hg line.

TABLE 1. SHORT TERM PRECISION AND DETECTION LIMIT FOR BENZENE ON TALMS I

N[a]	Samples Injected mL	µg	Date	Average Net Signal	Standard Dev.[b]	Relative Standard Dev.(%)	Pairwise t Calc.[c]	Pairwise t Critical[d]
11	1	350	3/82	24.7	4.6	19	-17.9	3.17
4	1	350	3/82	16.5	4.0	24	-8.22	5.84
6	1	350	11/82	65.1	3.3	5.	-48.9	4.03
5	0.5	175	3/82	8.36	2.2	26	-8.50	4.60
12	0.5	175	3/82	12.8	6.9	54	-5.89	3.11
18	0.5	175	3/82	18.7	9.2	49	-8.62	2.90
8	0.5	175	11/82	44.3	8.9	20	-14.0	3.50
6	0.3	105	11/82	34.1	9.0	26	-9.32	4.03
8	0.3	105	11/82	23.7	4.1	17	-16.3	3.50
13	0.25	88	3/82	8.06	3.5	43	-8.36	3.06
8	0.2	70	11/82	17.3	6.2	36	-7.93	3.50

[a] Number of injections.
[b] Standard deviation of net signal.
[c] Results of pairwise t-test of total signal vs. background.
[d] Tabulated value for 99.5% level.

TABLE 2. CALIBRATION DATA FOR BENZENE ON TALMS I

No. of Different Conc's.	Mass Range (μg)	Date	Slope[a]	Correlation Coefficient
4	350-1400	3/11/82	0.033	0.992
4	350-2800	3/12/82	0.038	0.997
4	175-1050	3/18/82	0.048	0.970
6	175-1050	3/26/82	0.032	0.990
4	175-1050	3/30/82	0.027	0.981
4	350-1750	4/08/82	0.083	0.976
4	350-3500	4/09/82	0.078	0.984
4	525-3500	4/13/82	0.030	0.997
4	525-3500	4/14/82	0.055	0.996
4	700-2800	4/15/82	0.059	1.000
5	700-3500	4/16/82	0.039	0.994
5	700-3500	11/2/82	0.024	0.999

[a] Slope of curve: Injected Volume = a (Signal) + b.

One of the important parameters in the analysis of organic compounds in air is the selectivity of the analysis for a given compound. High selectivity leads to unambiguous qualitative identification. Since TALMS uses a narrow atomic probe line, the resolution and selectivity should be very good. To test this, interference tests were run at the 253.7 nm mercury line with a number of organic compounds by repeatedly injecting headspace vapor from each compound in equilibrium with the liquid at room temperature. The total signals were pairwise t-tested vs. the background signal for each injection. The results are given in Table 3. Of the nine compounds tested, only o-xylene, monodeuterated benzene, pyridine, and toluene gave indications of interferences at the 99.5% probability level. The o-xylene interference is barely significant, and the monodeuterobenzene interference is only of academic interest. Preliminary tests conducted on 1,2,3-trichlorobenzene and phenol also gave no indication of interferences. Benzene impurities in the compounds studied could account for some positive interferences. However, the pyridine, o-xylene, toluene signals were negative relative to benzene. The interference signals from o-xylene, pyridine, and toluene were 2.8, 23, and 16% of the benzene signal on an equal volume basis.

To study the effects of temperature on the TALMS signal, the sample cell was enclosed in a Carle GC oven equipped with a thermocouple. Studies were conducted at 27 and 160°C with benzene, toluene, and pyridine by repeatedly injecting 10 ml of the compound studied at each temperature. The signals at each temperature were then pairwise t-tested for statistical significance. The results are given Table 4. The precision of the data at the higher temperatures is not very good due to problems with the temperature control. At the 99.5% significance level, all compounds show effects of temperature with 21, 50, and 57% increases in signal for benzene, pyridine, and toluene.

As expected in a prototype of any new equipment, some problems were encountered during the evaluation. The current controlled retardation plate (squeezer) originally supplied was not well constructed. It was the source of recurrent problems necessitating frequent repair and eventual replacement. Two modules, the PMT buffer log amplifier and the squeezer amplifier became inoperative and had to be exchanged. In addition, the signal generator and the squeezer D. C. clamp control developed defective components and were repaired inhouse. These components were damaged in a power outage and subsequent surge.

The sampling valves supplied with the instrument had large internal volumes, as did the attendant tubing. The plumbing system was revised, one valve was abandoned and the other replaced with a smaller solenoid valve before evaluation.

Problems of uncertain origin included frequent episodes of high noise levels and infrequently inability to attain proper wave forms on tune up. It was thought that these were due to irregularities in electrical power. In any case, both events were self-limiting conditions returning to normal without operator intervention.

TABLE 3. INTERFERENCES OF ORGANIC COMPOUNDS ON BENZENE TALMS I SIGNAL

Compound	Samples Injected[a] N	mL	Average Net Signal	Standard Dev.[b]	Pairwise t Calc.	Critical[c]	Interferences	Ratio[d] (%)
o-Xylene	10	10	-3.38	2.6	4.03	3.25	Yes	2.8
o-Chlorotoluene	10	10	0.43	5.4	-0.25	3.25		
Benzaldehyde	10	10	-0.03	2.3	0.25	3.25		
Naphthalene	10	10	0.83	4.0	-0.98	3.25		
2,4 Dichlorotoluene	10	10	3.52	4.9	-2.28	3.25		
Chlorobenzene	10	10	-2.67	5.8	1.45	3.25		
Monodeuterated-benzene	10	10	35.4	8.9	13.6	3.25	Yes	23
Pyridine	8	10	-346	18	52.6	3.50	Yes	20
Pyridine	8	10	-339	14	70.5	3.50	Yes	27
Toluene	6	20-40	-66.6	33	-4.94	4.03	Yes	16

[a] X mL of headspace gas injected N times.
[b] Standard deviation of average net signal.
[c] Tabulated t for 99.5% level.
[d] Ratio of average net interference signal to benzene signal for same volume.

TABLE 4. TEMPERATURE EFFECTS ON TALMS I SIGNALS

Compound	N[a]	TALMS Signal[b] 27°C	160°C	Change[c] (%)	Pairwise t Calc.[d]	Critical[e]
Benzene	10	261 ± 11	316 ± 43	21	-3.82	3.25
Pyridine	8	-339 ± 14	-684 ± 72	50	12.8	3.50
Toluene	6	-66.6 ± 33	-104 ± 48	57	6.11	4.03

[a] Number of injections of 10 mL.
[b] Average net signal at each temperature.
[c] Change relative to signal at 27°C.
[d] Calculated t value.
[e] Tabulated t value for 99.5% level.

SECTION 4

EVALUATION OF TALMS II

EQUIPMENT

The TALMS II instrument was developed as a compact benzene monitor for possible field use. It was much smaller than TALMS I with a height of 1 ft (30 cm), width of 1 ft (30 cm), and length of 3 ft (90 cm). The weight was 144 lbs (65 Kg). A photograph of the instrument is given in Figure 8. The major components were similar to those in TALMS I with two important exceptions. Since TALMS II was designed as a benzene monitor, it did not have a monochromator, although a compact one could be easily added. The other important difference was that TALMS II had a dual optical system with a beam splitter, a separate detector (PMT), and amplifier module to compensate for lamp and electronics drift.

As was the case in the TALMS I instrument, the optical components of the TALMS II were mounted on an optical bench attached to the base. A block diagram of the instrument is shown in Figure 9. The light source was a mercury Pen-Ray lamp contained in a Varian flange between the pole pieces of a permanent magnet with a field strength of 7 kilogauss. The polarization compensation plate was a quartz plate designed so that it might be rotated to any angle in the light beam. It was used to compensate for polarization imbalances from the source due to self-absorption. The current controlled phase retardation plate, or "squeezer," was the same type used in TALMS I.

The entrance to the beam splitter assembly was a straight section of tubing containing a 50 mm focal length lens and a linear polarizer. The beam splitter, a partially reflecting quartz plate, reflects some of the light to the reference PMT in a side arm.

Light reaches the sample cell through a 100 mm focal length lens. The cell is a Varian conflat 16 cm in length with a volume of 135 mL. Tubing extended from the end flanges of the cell to valves secured to the optical track. An additional 50 mm focal length lens was mounted where the cell was attached to the sample PMT.

Both reference and sample photomultiplier tubes were Hamamatsu R166 solar blind side-on tubes. Conventional mounts and dynode resistor networks were employed. Because of the narrow range of response of these photomultiplier tubes, 160 to 320 nm, it was not necessary to use a monochromator or bandpass filter in the instrument.

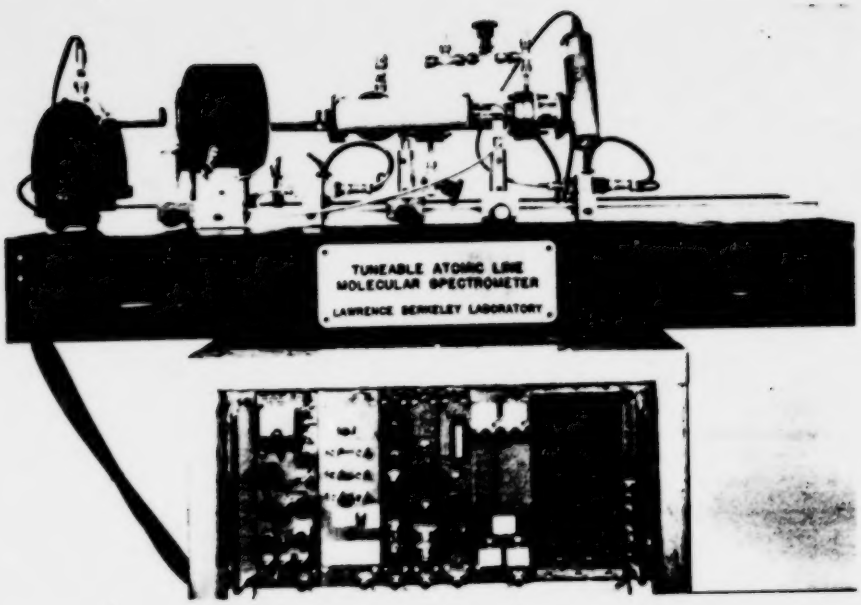

Figure 8. TALMS II instrumentation.

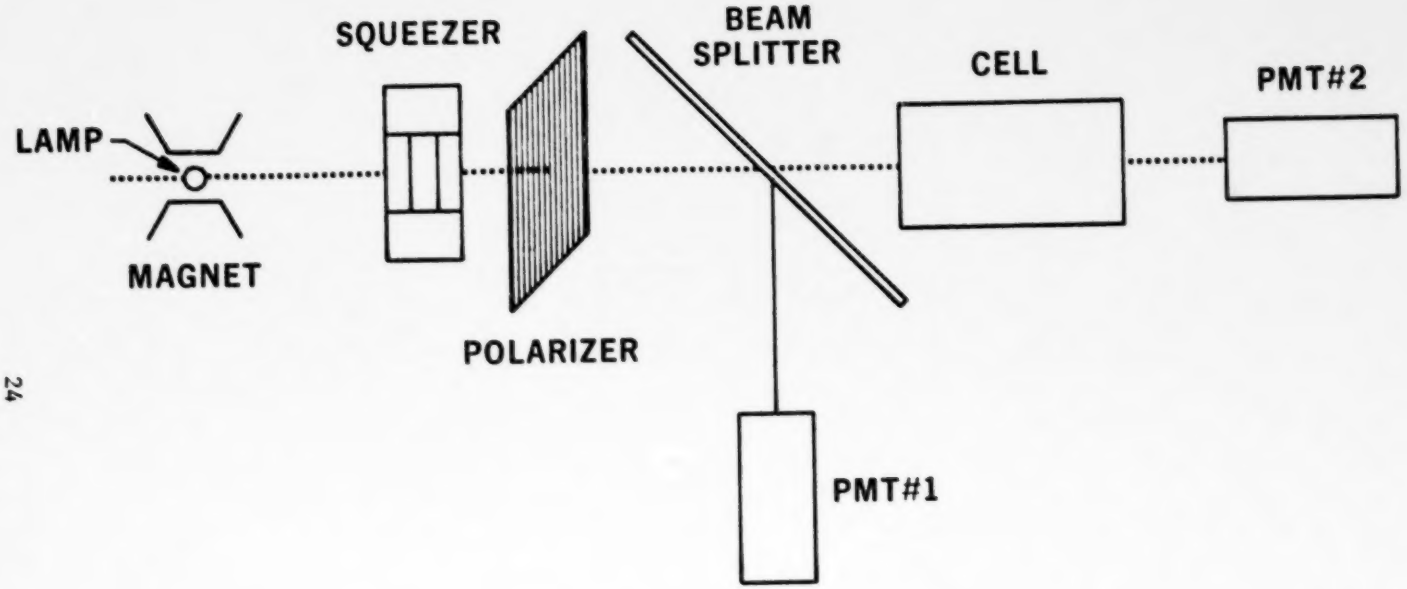

Figure 9. Block diagram of TALMS II.

The DC power supply and the power amplifiers for the light source and squeezer were mounted in a drawer in the base.

All other electronic modules were located in a small equipment rack, or NIM bin. These components and their functions are as follows:

AGC-PMT Module: The AGC-PMT Module supplies high voltage power to both photomultiplier tubes. The automatic gain control circuit maintains the high voltage to the PMT's at a constant level through a feed-back circuit so that the output from the PMT's are properly transformed by the logarithmic amplifiers. Front Panel - There is an on/off switch and voltage level control knob for each PMT. The labels "PMT 1" and "PMT 2" on the front panel correspond to the outputs labeled "PMT 1" and "PMT 2" on the rear panel. Rear Panel - The high voltage outputs for PMT 1 and PMT 2 are to be connected to the appropriate photomultiplier tube using the black high voltage BNC cables.

Squeezer Module: The Squeezer Module contains an audio frequency generator that provides the reference signal to the lock-in-amplifier and the AC signal to the squeezer power amplifier in the base of the TALMS monitor. The DC voltage control for the squeezer is also in this module. Front Panel - The meter on the front panel measures current to the squeezer. The knob labeled "variable" controls the current to the squeezer. The knob labeled "gain" varies the amplitude of the AC signal from the frequency generator that controls the AC power to the squeezer. The frequency is adjusted with the potentiometer labeled "freq". Rear Panel - The BNC output on the top of the rear panel supplies the reference signal to the lock-in amplifier and is to be connected to the "ref. in" input on the rear panel of the lock-in amplifier. It can also be used as a trigger source for an oscilloscope. The bottom BNC output is to be connected to the TALMS monitor end panel at "Input B".

Light Driver Module: The Light Driver Module provides the high frequency driving signal to the light source power amplifier in the base of the TALMS monitor. Front Panel - The potentiometer on the front panel labeled "frequency" varies the frequency of the signal to the power amplifier. The knob labeled "amplitude" varies the amplitude of the signal to the light source power amplifier. The amplitude knob can be locked by tightening the nut on the base of the shaft. Rear Panel - The BNC connector labeled "output" is to be connected to "Input A" on the end panel of the TALMS monitor. The BNC connector labeled "current" is to be connected to "current" on the end panel of the TALMS monitor.

Dual Beam Tracking Module: The Dual Beam Tracking Module accepts the input from PMT 1 and PMT 2. Each signal is passed through a logarithmic amplifier and then one signal is subtracted from the other in a difference amplifier. Front and Rear Panel - "Input 1" and "Input 2" on the module are to be connected to the BNC connectors on the back panel of the NIM Bin mainframe. They are labeled "1" and "2". The output labeled "AC diff output" is to be connected to the lock-in amplifier input labeled "sig in". The outputs labeled "buffer" are used to monitor the PMT signals before going through the log amplifier. The outputs labeled "log out" are used to

monitor the PMT signals after going through the logarithmic amplifier. On the front panel is a switch labeled "Ch. 2 log amp on/off". This is to be kept in the "on" position for normal operation. The off position is to be used when inserting external sample cells in the light beam for calibration purposes.

Lock-in Amplifier Module: The lock-in amplifier uses phase locked detection to extract the squeezer modulated signal from the photomultiplier tubes and provides a DC voltage output proportional to the sample concentration in the cell. Front Panel - To monitor signals in the lock-in amplifier, use the connector under the knob labeled "Monitor". Rear Panel - Connect "ref in" to the top BNC connector on the squeezer rear panel. Connect "sig in" to the "AC diff output" on the Dual Beam Tracking Module rear panel. Connect "output" to the "input" on the Time Constant Module.

Time Constant Module: The Time Constant Module will average the input signal over a given time interval. Front Panel - The selector knob selects 1, 10, 30, 50, and 100 second time averaging intervals. The button labeled "zero" will null the circuit in the module to begin averaging again. The "adjust" knob will add a DC offset to the output. The "input" and "output" can be connected through the front panel. Rear Panel - The "input" is to be connected to the "output" on the rear panel of the lock-in amplifier. The "output" is to be connected to a data collection device, e.g., a strip chart recorder.

The output was recorded on a Moseley 680 strip chart recorder, usually on the 50 mV scale.

The pump used to evacuate the cell was a Sargent-Welch 8803, rotary oil, portable, 25 L/min pump.

INSTRUMENT TUNE-UP PROCEDURES

The following procedures should be followed before use of the instrument or if the power has been off for an extended period of time.

1. Make sure the light source is on. If not, adjust the amplitude and frequency on the Light Driver Module until the output is stable. Do not overdrive the lamp since this causes reabsorption of the lamp output.

2. Remove the polarization compensation plate or turn it perpendicular to the light beam. Turn on the PMT power to both phototubes. Make sure the light beam is reaching PMT 1. Set the voltage on PMT 1 so that the output from the Dual Beam Tracking Module buffer for PMT 1 is about -3.0 volts. Adjust the mirror in the beam splitter to get maximum output from PMT 2. Set the voltage on PMT 2 so that the output is about -3.0 volts.

3. Monitor the buffer outputs on the Dual Beam Tracking Module for PMT 1 and PMT 2 on an oscilloscope. Look for an AC signal at about the 50 mv scale. If the sine waves are distorted, adjust the AC and DC controls

on the Squeezer Module until the maximum undistorted sine wave is obtained from PMT 1 and PMT 2. Adjust the PMT voltages so that the sine wave signals from both PMTs overlay exactly.

4. Turn the Channel 2 log amplifier switch off. Connect the oscilloscope to the "monitor out" jack on the lock-in amplifier, set the monitor knob to "ref", and adjust the reference frequency knob to get a maximum sine wave consistent with good wave form. Set the knob to "sig", and tune the sine wave signal to maximum. Set the knob to "mix", and adjust the phase control to full wave rectified form. Now turn the Channel 2 log amplifier switch on, and let the system stabilize.

5. Adjust the polarization compensation plate so that the signal from the buffer outputs of the Dual Beam Tracking Module are no longer sine waves but are now just a flat signal.

6. Set the meter on the lock-in amplifier to the 1 volt scale. Set the potentiometer to zero the meter. Set the time constant on the Time Constant Module to 30 if the 50 mv chart scale is used .

ANALYSIS PROCEDURES

The calibration procedures are identical to those used for TALMS I and described on page 14. The analysis procedures are essentially identical with those used for TALMS I. However, the peak height of the signal on a strip chart recorder, usually operated on the 50 mv scale, was used to measure the TALMS signal. A typical calibration curve is shown in Figure 10.

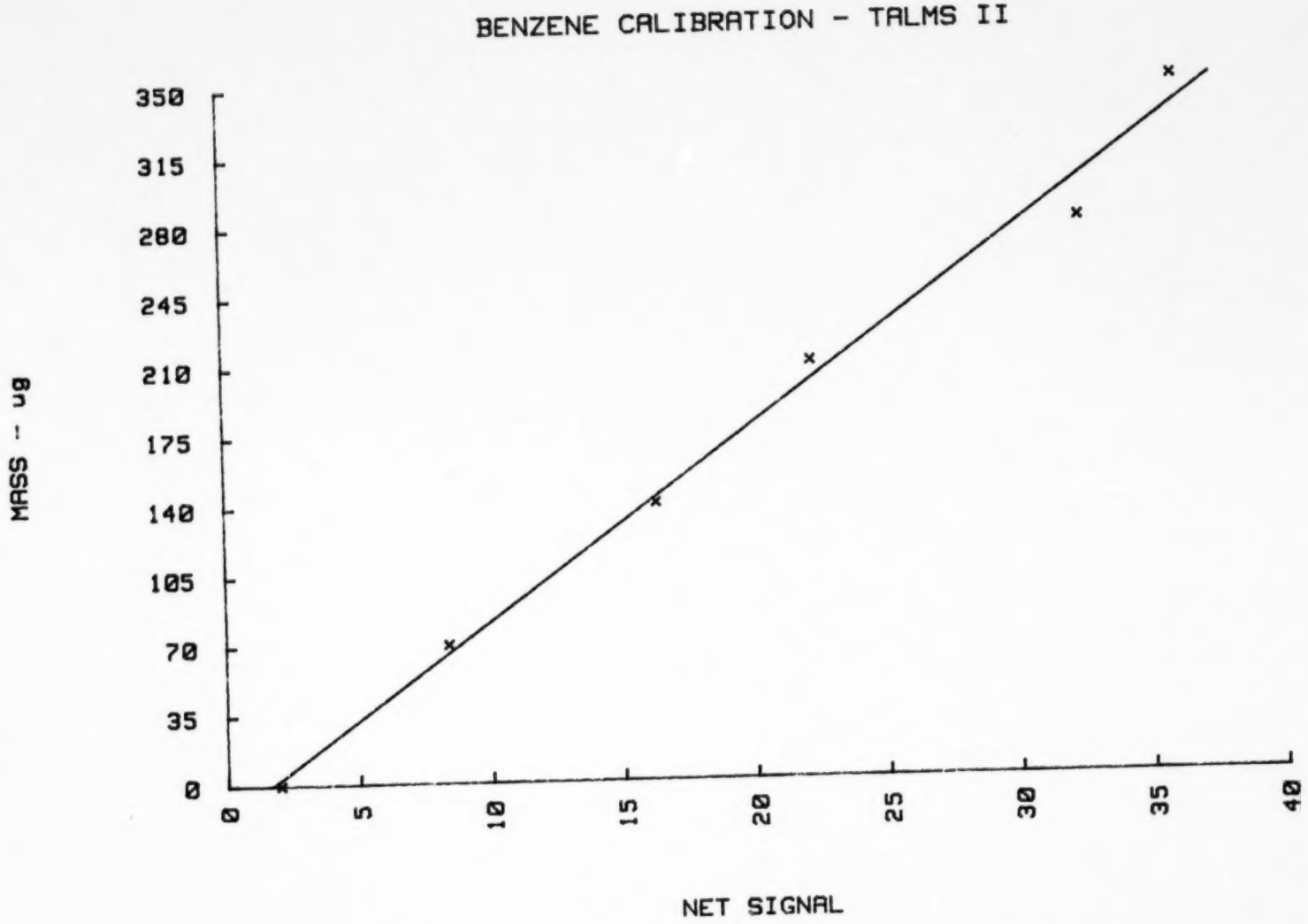

Figure 10. Benzene calibration curve for TALMS II.

RESULTS AND DISCUSSION

Evaluation tests were performed on TALMS II for detection limit; precision; calibration curve linearity and stability; interferences by other organic compounds; and effects of pressure. Preliminary tests with a National Bureau of Standards Reference Material for benzene and a cryogenic trap were also conducted.

The instrumental detection limit was determined by repeatedly injecting decreasing volumes of benzene headspace vapor ranging from 5 to 0.03 mL (1750 to 11 μg) in volume. The total signal for each injection was then pairwise t-tested vs. the background signal obtained with an empty cell. The resulting data are given in Table 5. The 0.03 mL volume, which was the smallest volume available, was significantly different at the 99.5% probability level from the background. Conservatively defining the detection limit as one-half this amount yields a mass of 6 μg. This is an improvement by a factor of six over the detection limit for TALMS I. Since the absorption cell is the same for both instruments, the improvement in the detection limit must be due to the dual beam system on TALMS II.

The relative standard deviation (precision) near the detection limit was 8.6-15%. Overall the precision ranged from 2.3 to 15%, relative standard deviation, with a median of 7.2%. This is a considerable improvement in precision over that found for TALMS I, proving the value of the dual beam system.

The slopes and correlation coefficients for calibration runs are listed in Table 6. For each run four or five different concentrations were injected in the range of 18 to 350 μg. The slopes of the calibration curves over a period of four months, expressed as volume injected (Y) vs. signal (X), were from 14.9 to 41.1, with a median of 17.6. The linearity of the curves as measured by the correlation coefficients for a linear fit ranged from 0.949 to 1.00, with a median of 0.997.

As with TALMS I, interference tests were run at the 253.7 nm mercury line with a number of organic compounds by repeatedly injecting headspace vapor from each compound in equilibrium with the liquid at room temperature. The total signals were pairwise t-tested vs. the background signal for each injection. Tests were run with ethylbenzene, o-xylene, benzaldehyde, and bromobenzene as well as the compounds listed in Table 7. For the four compounds given the interferences were less than one per cent, relative to an equal volume of benzene. During these tests it was found that essentially all compounds tested gave positive interferences in contradiction with the results on TALMS I. This problem was traced to high absorption levels leading to unstable TALMS signals. An automatic gain control (AGC) unit added to the instrument corrected the problem.

TABLE 5. SHORT TERM PRECISION AND DETECTION LIMIT FOR BENZENE ON TALMS II

N[a]	Samples Injected mL	µg	Date	Average Net Signal	Standard Dev.[b]	Relative Standard Dev.(%)	Pairwise t Calc.[c]	Pairwise t Critical[d]
7	5	1750	3/83	291	16	5.8	45.7	3.71
7	5	1750	3/83	312	9.1	2.9	90.7	3.71
8	5	1750	3/83	253	9.5	3.8	75.5	3.50
7	5	1750	3/83	224	9.0	4.0	65.7	3.71
6	5	1750	3/83	271	22	8.2	30.0	4.03
8	5	1750	4/83	244	11	4.5	62.7	3.50
5	1	350	2/83	57.6	1.6	2.8	40.2	4.60
6	1	350	5/83	60.6	1.4	2.3	106.	4.03
6	1	350	6/83	72.3	5.9	8.1	30.3	4.03
8	0.25	88	2/83	15.6	1.8	11	24.7	3.50
6	0.25	88	2/83	14.7	1.2	7.9	30.2	4.03
10	0.25	88	2/83	23.1	2.5	11	29.7	3.25
10	0.25	88	2/83	18.2	1.5	8.5	37.4	3.25
8	0.25	88	2/83	22.1	1.6	7.2	39.4	3.50
6	0.20	70	1/83	16.6	1.1	6.4	38.2	4.03
5	0.05	18	5/83	4.8	0.73	15	14.8	4.60
5	0.03	11	5/83	2.7	0.23	8.6	25.8	4.60

[a] Number of injections.
[b] Standard deviation of net signal.
[c] Results of pairwise t-test of total signal vs. background.
[d] Tabulated value for 99.5% level.

TABLE 6. CALIBRATION DATA FOR BENZENE ON TALMS II

No. of Different Conc's.	Mass Range (μg)	Date	Slope[a]	Correlation Coefficient
5	18-88	1/17/83	16.4	0.998
5	18-88	1/18/83	17.6	0.988
5	70-350	1/18/83	28.0	0.996
5	18-88	1/20/83	16.2	0.997
4	88-350	1/24/83	41.1	0.994
5	18-88	1/25/83	14.9	0.997
4	18-88	1/26/83	34.9	0.979
5	35-140	1/31/83	23.4	0.949
5	18-88	2/14/83	16.4	0.997
4	35-175	3/07/83	16.3	1.000
5	18-75	4/27/83	22.9	0.986

[a] Slope of curve: Volume Injected = a (Signal) + b

TABLE 7. INTERFERENCES OF ORGANIC COMPOUNDS ON BENZENE TALMS II SIGNAL

Compound	Samples Injected[a] N	mL	Average Net Signal	Standard Dev.[b]	Pairwise t Calc.	Critical[c]	Interferences	Ratio[d] (%)
Pyridine	6	5	-17.0	0.87	-47.8	4.03	Yes	5.6
Pyridine	5	5	-30.1	1.4	-50.1	4.60	Yes	8.3
Chlorobenzene	6	10	-2.9	0.27	-26.5	4.03	Yes	0.5
Chlorobenzene	5	10	-3.4	0.38	-19.9	4.60	Yes	0.5
Toluene	6	5	-5.1	0.69	-17.9	4.03	Yes	1.7
Toluene	5	5	-5.9	0.78	-17.0	4.60	Yes	1.6
Styrene	5	4	-14.9	2.5	-13.5	4.60	Yes	5.2

[a] Volume of headspace gas injected N times.
[b] Standard deviation of average net signal.
[c] Tabulated t for 99.5% level.
[d] Ratio of average net interference signal to benzene signal for same volume.

The data in Table 7 were obtained after the AGC unit was added to the instrument. Of the compounds tested pyridine, toluene, chlorobenzene, and styrene all gave negative interferences. This is in agreement with previous results on pyridine and toluene obtained with TALMS I. However, chlorobenzene was not found to give an interference with TALMS I. This is probably due to the small magnitude of the chlorobenzene interference, 0.5%. The interference signals from styrene, pyridine, and toluene were 5.2, 7.0, and 1.7% of the benzene signal on an equal volume basis. Since the interferences on TALMS II are considerably less than those found on TALMS I and are all negative, there is the possibility that they are due to artifacts caused by inaccuracies in signal processing. However, the user of the instrument must be aware of their potential existence. Since a mercury lamp is used as the source, any elemental mercury in the sample will cause a very large interference. A silver wool plug before the sample cell will prevent any mercury from entering the cell.

With sharp absorption features in the gas phase, there is a possibility of pressure broadening of the sharp feature, resulting in a possible decrease in intensity at the TALMS probe line. To study the effects of pressure on the TALMS signal, various sized samples were injected into the evacuated cell. Additions of benzene free air were then made to the cell, and the TALMS signal determined as the pressure increased. The pressure in the cell was adjusted from 3 to 636 torr. The results are given in Table 8. At a pressure of 66 torr the TALMS signal decreased by an average of 8%. As the pressure in the cell increased to 636 torr, the TALMS signal decreased by an average of 46%. This pressure effect must be compensated for if calibration samples and unknowns are analyzed at different pressures. The simplest solution is to calibrate and analyze at atmospheric pressure. This can be done by admitting clean air to fill the cell after addition of the sample.

Attempts were made to standardize the calibration data vs. the National Bureau of Standards Standard Reference Material 1806 which is 10 ppm-V benzene in nitrogen. Although the benzene in the SRM could be detected, the quantitation of the amount present could not be reliably performed.

Some preliminary experiments were performed to evaluate a cryogenic trap supplied with the instrument. This was essentially a ½ in OD copper tube, six inches in length, packed with copper turnings and equipped with heated inlet and outlet side arms (¼ in OD). It was designed to operate with liquid nitrogen as the cryogenic fluid. Due to leaks in the trap and noisy instrument performance during this period, these experiments were not successful.

Compared to TALMS I, very few problems were encountered with TALMS II, except for the one which lead to the addition of the automatic gain control module. The power to the unit was left on for months, and the unit was moved twice during the year. One mercury lamp burned out during this period. After one relocation persistent noise appeared which was later traced to a bad connection in the electronics modules. An operational amplifier on the PMT control unit and a dynode resistor in the PMT network were also replaced during the year. The tubing connecting the valves and the sample cell supplied with the instrument was shortened to reduce the volume of the cell system.

TABLE 8. PRESSURE EFFECT ON BENZENE TALMS II SIGNAL

Pressure[a] (Torr)	TALMS Signal[b] (%) Sample Size (μg) 100	400	2000	Median (%)
3	100	100	100	100
66	91	92	93	92
130	67	--	84	75
320	42	62	74	62
478	--	--	64	--
636	34	54	65	54

[a] Calculated from volume injected, cell volume, and temperature.
[b] Relative to value at 3 Torr set as 100%.

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